The residues were analyzed by pmr. The results are reported in Table II.

Isomerization of 9 and 10. A.—A solution of **9** (0.40 g, 1.0 mmol) in $CHCl_3$ (3 ml) was treated with a 1 *M* solution of Br_2 in $CHCl_3$ (1 ml). After standing at room temperature in the dark for 100 hr, the solution was poured into saturated aqueous $NaHSO_3$; the organic layer was washed with water, dried, and evaporated. The pmr spectrum of the crude product showed the signals of **9** and **10** in the ratio 55:45; a third signal at δ 4.3 (doublet of doublets, W = 18 Hz) was also present (<5%). In contrast **10** was recovered unchanged after identical treatment with Br_2.

B.—A solution of **9** (0.40 g, 1.0 mmol) in Et_2O (3 ml) was treated with a 1 *M* solution of Br_2 in $CHCl_3$ (1 ml), left at room temperature in the dark for 100 hr, and worked up as described under A. The pmr spectrum of the crude reaction mixture indicated the presence of **9** and **10** in the ratio 73:27.

C.—A solution of **9** (0.40 g) in $CHCl_3$ (4 ml) was saturated with dry HBr and left at room temperature for 100 hr. After washing with water and saturated aqueous $NaHCO_3$, drying, and evaporation, unchanged **9** (ir and pmr) was recovered.

Treatment of 7 with HBr.—A solution of **7** (0.13 g) in $CHCl_3$ (5 ml) was saturated with dry HBr and left at room temperature for 3 hr. After washing with water, saturated aqueous $NaHCO_3$, and water, drying, and evaporation, a solid residue (0.14 g) was obtained, consisting of **5** accompanied by a small amount (~3%) of the isomer **6** (pmr). The dibromide **5** was recovered unchanged after standing for 15 hr in a $CHCl_3$ solution saturated with dry HBr.

Acknowledgments.—We wish to thank Professor G. Berti for helpful discussion. This work was supported in part by a grant from Consiglio Nazionale delle Ricerche.

Registry No.—**4**, 771-98-2; **5**, 40940-62-3; **7**, 40940-63-4; **8**, 40940-64-5; **9**, 40940-65-6; **10**, 40940-66-7.

Stereochemistry of the Acid-Catalyzed Cyclization of 2-(3-Butenyl)-1-phenylcyclohexanols

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Acid-catalyzed cyclization of the phenyl-substituted alcohols **4** and **5** was shown to give cis-fused bicyclic formates with no detectable amount of trans-fused products. Since cyclization in deuterioformic acid led to no incorporation of deuterium into the cyclic product, intervention of cyclohexenyl intermediates cannot be involved in the reaction. This divergence from results obtained with other substituted cyclohexanols is considered to be a direct consequence of steric interactions involving the bulky and geometrically anisotropic phenyl group. The results show that the substituent at the cationic carbon in acid-catalyzed olefin cyclizations may significantly alter the mechanism and stereochemistry of acid-catalyzed olefin cyclizations.

Olefinic cyclizations have recently become established as a key method for the construction of complex polycyclic compounds. In the course of a model study[1] on the stereochemistry and mechanisms of biogenetic-like olefin cyclizations, we have prepared and studied the acid-catalyzed cyclization of several 2-alkenylcyclohexane systems such as **1**, **2**, and **3**. We have now examined the cyclization of the related benzylic alcohols **4** and **5**. Although not directly relevant to biogenetic systems,[2] these cyclizations are of particular interest since the results are directly divergent from those obtained with previously studied systems.

The synthesis of the cyclization substrates is outlined in Chart I. Spectral and chromatographic data gave evidence for the presence of only one isomer in the product obtained from reaction of phenylmagnesium bromide with ketone **6**. By analogy with the reaction of 2-alkylcyclohexanones with Grignard reagents,[3] this

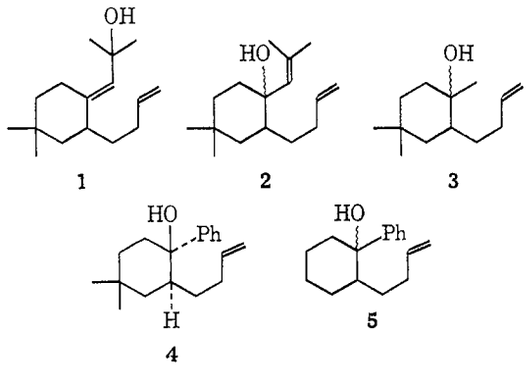
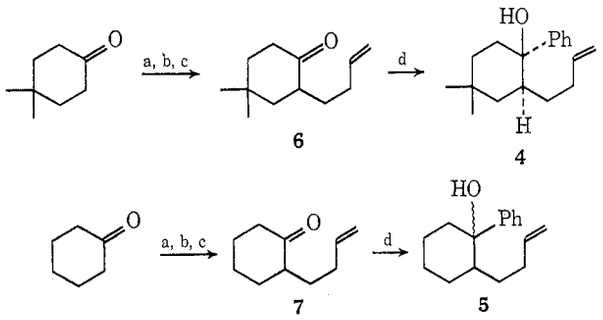


CHART I

SYNTHESIS OF CYCLIZATION ALCOHOLS[a]



[a] a, cyclohexylamine, $-H_2O$; b, EtMgBr; c, $CH_2{=}CH{-}CH_2CH_2X$; d, C_6H_5MgBr.

(1) Other papers in this series follow: (a) K. E. Harding, R. C. Ligon, T.-C. Wu, and L. Rode, *J. Amer. Chem. Soc.*, **94**, 6245 (1972); (b) K. E. Harding, *Bioorg. Chem.*, **2**, 248 (1973).

(2) Cyclization of alcohol **4** was considered of interest in relation to other biogenetic-like olefin cyclizations because the phenyl group might be expected to stabilize the intermediate cyclohexyl cation and thus reduce elimination–reprotonation reactions known to complicate many early attempts to examine cyclizations of cyclohexyl cations.[1b] However, it was recognized from the beginning that this alcohol was less satisfactory than alcohol **1** as a model compound because of the increased steric factors present with a phenyl substituent.

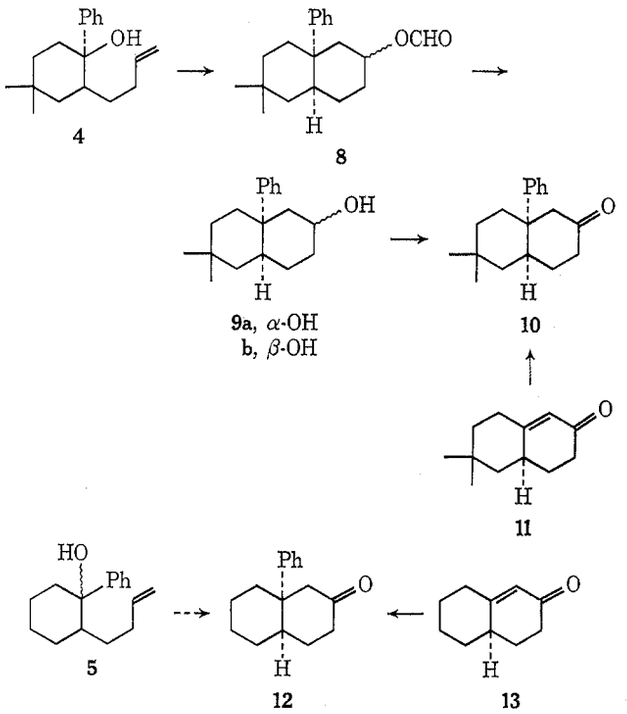
(3) J. R. Luderer, J. E. Woodall, and J. L. Pyle, *J. Org. Chem.*, **36**, 2909 (1971); J. Ficini and A. Maujean, *C. R. Acad. Sci., Ser. C*, **266**, 227 (1968).

alcohol has been assigned the trans structure **4**.[4] Since alcohols **4** and **5** were tertiary benzylic alcohols, the crude alcohols were used directly in the cyclization studies.

Treatment of alcohol **4** with either 97% or anhydrous formic acid[7] at room temperature for 1 hr gave bicyclic formates (**8**) in high yield (Chart II). By thin

CHART II

CYCLIZATION REACTIONS AND COMPARISON COMPOUNDS



layer chromatography, the crude product was separated into a hydrocarbon fraction (15% yield) and a formate fraction (80% yield). The hydrocarbon fraction did not lead to additional formates upon retreatment with formic acid and was not investigated further. The nmr spectrum of the formate fraction indicated that it was a mixture. Three singlet absorptions for methyl groups were observed (δ 1.01, 1.00, and 0.96 ppm). Cleavage of the formate ester group with lithium aluminum hydride gave the corresponding alcohols (**9**) in quantitative yield. The product mixture was separated by preparative layer chromatography on silica gel into equal amounts of two isomeric alcohols. The nmr spectrum of the alcohol with lower R_f showed a single absorption at δ 0.99 ppm for the geminal dimethyl group and a multiplet at δ 3.24 ppm with a $W_{1/2}$ of 18 Hz. The spectrum of the other alcohol showed absorption at δ 0.93 and 0.98 ppm for the two methyl groups and a multiplet at δ 3.90 ppm with a $W_{1/2}$ of 10 Hz. Proof that these alcohols were isomeric only at the carbon bearing the hydroxyl group was obtained by Jones oxidation of the individual alcohols and of the mixture to give a single ketonic product (**10**).

Oxidation of the mixture of alcohols gave ketone **10** in a crude yield of 85%. Analysis by gc on two columns showed only one long retention time peak. No evidence for an isomeric ketone was obtained. Recrystallization from hexane gave pure ketone **10**, mp 84–85°.

The structure and stereochemistry of this ketone were proven by comparison with material synthesized by an independent route. Addition of methyl vinyl ketone to the pyrrolidine enamine of 4,4-dimethylcyclohexanone gave the dimethyloctalone **11**. Addition of phenylmagnesium bromide to octalone **11** in the presence of 1 mol % of cuprous bromide gave decalone **10**, identical (melting point, ir, gc) with the ketone obtained from the cyclization reaction. The cis stereochemistry of phenyldecalone products obtained by conjugate addition to $\Delta^{1,9}$-2-octalone has been previously established.[8]

The mechanism of this cyclization of alcohol **4** was investigated by conducting the cyclization in deuterioformic acid.[9] A 50-mg sample of alcohol **4** was treated with 1 ml of deuterioformic acid at room temperature for 2 hr. The product was isolated and converted to crystalline ketone **10** in the normal manner. Mass spectral analysis of the ketone isolated from this cyclization showed no measurable incorporation of deuterium. This result proves that product formation is not occurring by deprotonation to a cyclohexenyl intermediate followed by reprotonation and cyclization.

Results from cyclization of alcohol **5** were consistent with those obtained with alcohol **4**. Alcohol **5** consisted of both epimeric alcohols as evidenced by thin layer chromatography. This mixture was converted into bicyclic formates in high yield upon treatment with formic acid at room temperature. Hydrolysis and oxidation gave the phenyldecalone **12**. No evidence was found for the isomeric trans product. Addition of phenylmagnesium bromide to $\Delta^{1,9}$-2-octalone gave authentic *cis*-9-phenyl-2-decalone (**12**), identical (gc, ir, melting point) with the decalone obtained from the cyclization reaction.

Discussion

The most notable features in the cyclizations of alcohols **4** and **5** are the essentially exclusive formation of cis-fused decalin products and the absence of cyclohexenes as intermediates in the reaction. Comparison of these results with results from cyclization of other 1-substituted cyclohexanols illustrates the influence of the phenyl substituent. Cyclizations of 1-methylcyclohexanols involve considerable elimination to cyclohexenyl intermediates.[10,11] For example, cyclization of alcohol **3** gives predominantly cis-fused products with predominant incorporation of one or more deuterium atoms.[12] In the cases of alcohols **1** and **2**, where

(4) Spectral evidence consistent with this assignment has been obtained from nmr studies. The spectrum of alcohol **4** shows no methylene absorption below δ 2.0. An axial phenyl group on a cyclohexane has been shown to shift the C-2 and C-6 equatorial protons to significantly below δ 2.0 in several cases.[5,6] Use of lanthanide shift reagents did not simplify the spectrum sufficiently to allow unequivocal assignment of stereochemistry.

(5) P. J. Beeby and S. Sternhell, *Aust. J. Chem.*, **24**, 809 (1971).

(6) E. W. Garbisch, Jr., and D. B. Patterson, *J. Amer. Chem. Soc.*, **85**, 3228 (1963).

(7) H. I. Schlesinger and A. W. Martin, *J. Amer. Chem. Soc.*, **36**, 1589 (1914).

(8) S. M. McElvain and D. C. Remy, *J. Amer. Chem. Soc.*, **82**, 3960 (1960).

(9) We thank Mr. David Bailey for conducting this experiment.

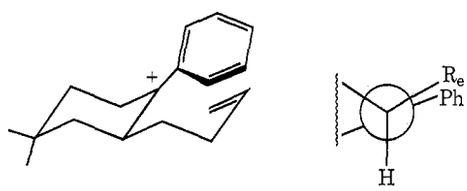
(10) P. T. Lansbury, *Accounts Chem. Res.*, **5**, 311 (1972), and references cited therein.

(11) D. C. Hibbit and R. P. Linstead, *J. Chem. Soc.*, 470 (1936); unpublished observations of W. S. Johnson and H. D. Doshan, see H. D. Doshan, Ph.D. Dissertation, Stanford University, 1968.

(12) K. Harding, R. C. Ligon, and W. D. Nash, unpublished observations.

elimination to cyclohexenyl intermediates is not observed, more than 90% of the cyclization product is trans fused.[1,12] This stereochemical divergence of the results obtained with alcohols **4** and **5** from results with other cyclohexanols eliminates their use as models for biogenetic-like olefin cyclizations.

Although the data available are insufficient to allow definitive rationalization for the stereochemistry of these cyclizations, the anomalous effect of the phenyl group may be considered to be a logical consequence of the steric requirements of the phenyl substituent. The normal conformation[13] for an intermediate cyclohexyl cation (**14**) would require either very large steric strain



14

of the $A^{1,3}$ type[11b] or rotation of the phenyl group resulting in loss of resonance stabilization of the catonic carbon. The unfavorable interactions present in structure **14** could be relieved in a number of ways. Conformational inversion to the alternate chair form,[14] conversion to a flexible conformation, flattening of the chair in cation **14** at C_2–C_1–C_6, or bending of the C_1–phenyl bond to give a nonplanar cationic carbon would result in such relief. Each of these conformations might be expected to lead to cis products preferentially.

In addition, the relative stabilities of the *cis*- and *trans*-9-phenyldecalin systems are not known, and the geometric anisotropy[15] of the phenyl group prevents use of *A* values to estimate stabilities in the manner used for methyldecalins. Thus the potential effect of the relative stabilities of the initially formed bicyclic cations upon the stereochemistry of the cyclization cannot be evaluated.

Experimental Section

Melting points were taken in open capillary tubes. Ir spectra were determined with a Perkin-Elmer Model 237 spectrophotometer. Nmr spectra were obtained with Varian Associates T-60 or HA-100 spectrometers operating at 60 or 100 MHz, respectively. Chemical shifts (δ) are reported in parts per million downfield with tetramethylsilane (TMS) as internal standard. Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz. High-resolution mass spectra were obtained on a CEC Model 21-110 spectrometer under the supervision of Dr. R. Grigsby. Evaporative distillation refers to bulb-to-bulb (Kugelrohr) short-path distillation. The temperatures cited for these distillations are the maximum temperature of the oven during the distillation.

4,4-Dimethylcyclohexanone.—This compound was prepared by hydrogenation of 4,4-dimethyl-2-cyclohexenone prepared according to the procedure of Dauben.[16] Thus, 30 g (0.242 mol) of 4,4-dimethyl-2-cyclohexenone, 3 g of 5% palladium-on-charcoal catalyst, and 600 ml of absolute ethanol were placed in a 1000-ml flask. The hydrogenation was conducted with a sloping-manifold atmospheric-pressure hydrogenator. After hydrogenation was complete, the hydrogenator was flushed with nitrogen and the catalyst was removed by filtration. About 25 ml of 10% hydrochloric acid was slowly added to the filtrate, followed by 1200 ml of water. The mixture was then extracted with ether. The combined ether extracts were washed several times with water, bicarbonate, and brine, dried over anhydrous sodium sulfate, and concentrated to give 23.43 g (77% yield) of white crystals: mp 41–43° (reported mp 40–42°,[17] 38–41°[18]); ir (CCl_4) 1703 (carbonyl), 2950 ($-CH_3$), 1450 ($-CH_2-$), and the absence of 3020 and 800 cm^{-1} (–CH=CH–) peaks; nmr (CCl_4, 60 MHz) δ 1.1 (s, 6 H, geminal methyls), 1.5–1.85 (m, 4 H, methylenes), and 2.1–2.5 ppm (m, 4 H, α-methylenes).

2-(3-Butenyl)-4,4-dimethylcyclohexanone (6).—The procedure described by Stork and Dowd[19] for similar alkylations was slightly modified. Therefore, 1.8 g (8.7 mmol) of *N*-cyclohexyl-4,4-dimethylcyclohexylimine, prepared in the normal manner from 4,4-dimethylcyclohexanone, in 15 ml of tetrahydrofuran was added dropwise to a cold and stirred solution of 12 ml of 1 *M* ethylmagnesium bromide in tetrahydrofuran. The mixture was heated to reflux for 5 hr under nitrogen; then a solution of 1.9 g (9.1 mmol) of 3-butenyl tosylate,[20] prepared from 3-buten-1-ol,[21] in 15 ml of tetrahydrofuran was added dropwise. The reaction mixture was refluxed overnight and the imine salts were decomposed by dropwise addition of 9 ml of 10% hydrochloric acid solution and sufficient water to dissolve the precipitate. The aqueous solution was extracted with ether. The combined organic phases were washed (acid, bicarbonate, and brine), dried over anhydrous sodium sulfate, concentrated, and evaporatively distilled (0.18 mm, 86°) to give 1.2 g (77% yield) of ketone **6**: ir (film) 1703 (carbonyl), 1628, 986, and 910 cm^{-1} ($-CH=CH_2$); nmr (CCl_4, 60 MHz) δ 1.0 (s, 3 H, methyl), 1.2 (s, 3 H, methyl), 4.6–5.2 (m, 2 H, $-CH=CH_2$), and 5.4–6.0 ppm (m, 1 H, $-CH=CH_2$).

The ketone was about 95% pure with the presence of a small amount of unalkylated ketone shown by gc (Carbowax, 178°). The oxime was prepared and recrystallized twice as white microcrystals from ethanol–water solution, mp 83–83.5°.

Anal. Calcd for $C_{12}H_{21}ON$: C, 73.78; H, 10.84; N, 7.17. Found: C, 73.75; H, 10.78; N, 7.03.

1-Phenyl-2-(3-butenyl)-4,4-dimethylcyclohexanol (4).—A solution of 200 mg (1.11 mmol) of ketone **6** in 2 ml of anhydrous ether was added dropwise to 10 ml of a stirred 1 *M* solution of phenylmagnesium bromide in tetrahydrofuran. The solution was stirred under nitrogen for 11 hr, poured into water, and extracted with ether. The combined extracts were washed (water, bicarbonate, and brine), dried over magnesium sulfate, and concentrated to give 351 mg of a yellow oil. Chromatography over 12 g of silica gel to remove biphenyl gave 287 mg (100% crude yield) of alcohol **4**: ir (film) 3430 cm^{-1} (OH); nmr (CCl_4, 100 MHz) δ 0.99 and 1.01 (singlets, geminal methyls), 4.65–4.95 (m, 2 H, $-CH=CH_2$), 5.25–5.80 (m, 1 H, $-CH=CH_2$), and 7.28 ppm (m, 5 H, phenyl).

All spectral and chromatographic evidence for alcohol **4** indicated that it was a single isomer.

Cyclization of Alcohol 4.—A 200-mg sample (0.775 mmol) of alcohol **4** was dissolved in 30 ml of 97% formic acid and stirred at room temperature for 1 hr. The solution was poured into 150 ml of water and extracted three times with 50 ml of ether. The ether extracts were washed (water, bicarbonate, and brine), dried over $MgSO_4$, and concentrated to yield 226 mg of a yellow oil. Preparative tlc gave 28 mg of hydrocarbons and 174 mg (79% yield) of formate esters. The nmr spectrum (CCl_4, 100 MHz) exhibited three distinct methyl signals as singlets at δ 0.87, 0.98, and 1.02 ppm.

A 100-mg sample of the hydrocarbon fractions obtained from several of the above cyclizations was retreated with 15 ml of 97% formic acid at room temperature for 24 hr. Analysis by tlc and nmr indicated that no significant conversion to nonhydrocarbon products occurred.

A 200-mg sample of the formate ester fraction was dissolved in anhydrous ether and added to an excess of a stirred solution of

(13) (a) F. R. Jensen, L. H. Gale, and J. E. Rodgers, *J. Amer. Chem. Soc.*, **90**, 5793 (1968); (b) F. Johnson, *Chem. Rev.*, **68**, 375 (1968).

(14) This conformation is a very probable structure for the cationic intermediate in the cyclization of alcohol **5**. However, in the case of alcohol **4**, this conformation would contain a quite unfavorable 1,3-diaxial interaction between the butenyl side chain and the axial C-4 methyl.

(15) N. L. Allinger and M. T. Tribble, *Tetrahedron Lett.*, 3259 (1971); S. Sicsic and Z. Welvart, *Chem. Commun.*, 499 (1966).

(16) W. G. Dauben, G. W. Shaffer, and N. D. Vietmeyer, *J. Org. Chem.*, **33**, 4060 (1968).

(17) R. F. Miller and R. Adams, *J. Amer. Chem. Soc.*, **58**, 787 (1936).

(18) E. B. Reid and T. E. Gompf, *J. Org. Chem.*, **18**, 661 (1953).

(19) G. Stork and S. R. Dowd, *J. Amer. Chem. Soc.*, **85**, 2178 (1963).

(20) K. L. Servis and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 3773 (1964).

(21) R. B. Kinnel, B. B. Molloy, D. W. Graham, and K. E. Harding, *Org. Prep. Proced. Int.*, **4**, 27 (1972).

lithium aluminum hydride in ether. The solution was stirred at room temperature for 30 min. Isolation of product in the normal manner gave 180 mg (100% crude yield) of alcoholic product. Preparative tlc gave 68 mg of alcohol **9a**, nmr (CCl_4, 60 MHz) δ 0.87 (s, geminal methyl), 0.97 (s, geminal methyl), 3.79 (m, $W_{1/2}$ = 18 Hz, 1H, -CHO-), and 7.22 ppm (m, 5 H, phenyl), and 73 mg of alcohol **9b**, δ 0.98 (s, geminal methyls), 3.47 (m, $W_{1/2}$ = 18 Hz, 1 H, -CHO-), and 7.22 ppm (m, 5 H, phenyl).

A 100-mg sample of the crude alcohol mixture was dissolved in 5 ml of acetone and treated with an excess of Jones reagent.[22] The resulting product (85 mg) was subjected to evaporative distillation (0.07 mm, 130°) to give 80 mg (81% yield) of ketone **10**. Analysis by gc indicated the presence of only one ketonic component. Recrystallization from hexane gave pure ketone **10**: mp 85–86°; ir (KBr) 1690 cm^{-1} (carbonyl); nmr (CCl_4, 60 MHz) δ 1.05 and 1.15 (singlets, geminal methyls).

Anal. Calcd for $C_{18}H_{24}O$: C, 84.76; H, 9.02. Found: C, 84.76; H, 9.10.

Oxidation of alcohols **9a** and **9b** separately gave only ketone **10** in each case. The infrared spectrum of this ketone was essentially identical with the corresponding spectrum of authentic *cis*-6,6-dimethyl-9-phenyl-2-decalone, prepared as described below.

Cyclization of alcohol **4** in anhydrous formic acid[7] gave results indistinguishable from those described above using 97% formic acid.

Cyclization of Alcohol 4 in Deuterioformic Acid.—A 50-mg sample of alcohol **4** was treated with 1 ml of deuterioformic acid (98%, Merck Sharp and Dohme) for 2 hr at room temperature. Work-up as in the above cyclizations gave 50 mg of crude product. The product was treated with lithium aluminum hydride and then with Jones reagent to convert the product to ketone **10**. The mass spectrum of this ketone was essentially identical with that of authentic ketone **10**. In particular, the ratios of peaks at *m/e* 256 (P^+) and 257 ($P^+ + 1$) were indistinguishable.

2-(3-Butenyl)cyclohexanone (7).—The procedure described for the preparation of ketone **6** was used. Thus a solution of 5.37 g (0.03 mol) of *N*-cyclohexylcyclohexylimine, prepared in the normal manner from cyclohexanone, in 10 ml of tetrahydrofuran was added dropwise to a cold and stirred solution of 30 ml of 1.0 *M* ethylmagnesium bromide in tetrahydrofuran. The mixture was heated at reflux for 5 hr under nitrogen; then a solution of 4.05 g (0.03 mol) of 4-bromo-1-butene in 10 ml of tetrahydrofuran was added dropwise. The reaction mixture was refluxed overnight, and then the imine salts were decomposed by dropwise addition of 30 ml of 10% hydrochloric acid solution and sufficient water to dissolve the precipitate. The aqueous solution was extracted with ether. The combined organic phases were washed (acid, bicarbonate, and brine), dried over anhydrous sodium sulfate, concentrated, and distilled through a short-path apparatus to give 3.37 g (73% yield) of the desired ketone as a colorless liquid: bp 95–105° (0.3 mm) [lit.[11] bp 41–42° (0.007 mm)]; ir (film) 1703 (carbonyl group), 1628, 986, and 910 cm^{-1} (-CH=CH_2); nmr (CCl_4, 60 MHz) δ 0.7–2.58 (m, 13 H), 4.65–5.25 (m, 2 H, -CH=CH_2), and 5.3–6.3 ppm (m, 1 H, -CH=CH_2). The material was 98% pure by gc (Carbowax, 140°).

1-Phenyl-2-(3-butenyl)cyclohexanol (5).—A solution of 1.0 g (6.60 mmol) of 2-(3-butenyl)cyclohexanone in 10 ml of tetrahydrofuran was added dropwise into a stirred solution of 33 ml of 1 *M* phenylmagnesium bromide in tetrahydrofuran under nitrogen. After the mixture was stirred at room temperature for 6 hr, it was poured into ice-cold water and allowed to stand for 1.5 hr. The mixture was extracted with ether, and the ether extracts were washed (bicarbonate and brine), dried over magnesium sulfate, and concentrated. The biphenyl was removed by column chromatography to give 1.36 g (90% yield) of alcohol **5**: ir (film) 3400 (broad, -OH), 3030, 980, 910 (-CH=CH_2), 1580, 1490, 760, and 705 cm^{-1} (-C_6H_5); nmr (CCl_4, 60 MHz) δ 4.5–5.0 (m, 2 H, -CH=CH_2), 5.1–5.9 (m, 1 H, -CH=CH_2), and 7.30 ppm (m, 5 H, aromatic H).

Cyclization of Alcohol 5.—A 0.93-g (4.04 mmol) sample of alcohol **5** was treated at room temperature with 100 ml of 97% formic acid for 5 hr. The mixture was poured into water and extracted with ether. The combined ether extracts were washed (water, bicarbonate, and brine), dried over sodium sulfate, and concentrated to give 1.04 g (100% yield) of cyclic formates: ir (film) 1720 cm^{-1} (C=O).

The crude cyclic product was converted by formate ester cleavage and Jones oxidation into the corresponding ketone in the same manner as described for the cyclization of alcohol **4**. Analysis of the product by gc showed a single ketonic component identical in retention time with authentic *cis*-9-phenyl-2-decalone. Recrystallization of the ketone from hexane gave pure ketone **12**: mp 68–69°; ir (film) 1703 cm^{-1} (C=O). The infrared spectrum of this ketone was essentially identical with the spectrum of authentic *cis*-9-phenyl-2-decalone, prepared as described below.

6,6-Dimethyl-$\Delta^{1,9}$-2-octalone (11).—A solution of methyl vinyl ketone (1.42 g, 0.021 mol) in 20 ml of dry benzene was added to a solution of 2.62 g (0.0146 mol) of 1-pyrolidino-4,4-dimethylcyclohexene [bp 86–89° (1.4 mm)] prepared in the normal manner from pyrolidine and 4,4-dimethylcyclohexanone. The mixture was refluxed for 4 hr; 70 ml of water was added, and refluxing was continued for an additional 16 hr. The cooled reaction mixture was diluted with water and extracted with ether. The combined ether extracts were washed (3 *N* HCl, bicarbonate, and brine), dried over magnesium sulfate, concentrated, and evaporatively distilled (0.35 mm, 100°) to give 1.18 g (44% yield) of octalone **11**. Recrystallization gave pure octalone **11** as fine transparent needles: mp 72.5–73°; ir (CCl_4) 1670 (C=O) and 1620 cm^{-1} (C=C); nmr (CCl_4, 60 MHz) δ 0.96 and 1.06 (singlets, geminal methyls) and 5.72 ppm (s, vinyl H).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.55; H, 10.05.

6,6-Dimethyl-9-phenyl-2-decalone (10).—A solution of 0.78 g (4.23 mmol) of 6,6-dimethyl-$\Delta^{1,9}$-2-octalone in 10 ml of anhydrous ether was added dropwise to 4.5 ml of an ice cold, stirred solution of 1 *M* phenylmagnesium bromide in ether containing 0.02 g of cuprous bromide. The reaction mixture was kept at 0° for 30 min, brought to room temperature, and stirred for an additional 1 hr. The reaction mixture was poured onto an ice–acetic acid mixture and extracted with ether. The combined ether extracts were washed (bicarbonate and brine), dried, concentrated, and distilled. Purification by thin layer chromatography and recrystallization gave pure decalone **10**: mp 85–86°; ir (CCl_4) 1705 cm^{-1} (C=O); nmr (CCl_4, 60 MHz) δ 1.05 and 1.15 (singlets, geminal methyls) and 7.15 ppm (m, 5 H, phenyl).

9-Phenyl-2-decalone (12).—The procedure of McElvain and Remy[8] was modified slightly. A solution of 0.5 g (3.3 mmol) of $\Delta^{1,9}$-2-octalone (**13**)[23,24] in 10 ml of anhydrous ether was added dropwise to 4 ml of an ice-cold, stirred 1 *M* solution of phenylmagnesium bromide in ether containing 0.02 g of cuprous bromide. The reaction mixture was kept at 0° for 30 min, brought to room temperature for 1 hr, poured onto an ice–acetic acid mixture, and extracted with ether. The combined ether extracts were washed (bicarbonate and brine), concentrated, and distilled. Purification by tlc and recrystallization gave pure decalone **12**: mp 68–68.5° (lit.[8] mp 68–69°); ir (film) 1703 cm^{-1} (C=O).

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Registry No.—**4**, 41163-76-2; **5**, 41171-98-6; **6**, 38481-13-9; 6 oxime, 38481-22-0; **7**, 16178-83-9; **9a**, 41163-77-3; **9b**, 41163-78-4; **10**, 41163-79-5; **11**, 4044-27-3; **12**, 41163-80-8; 4,4-dimethylcyclohexanone, 4255-62-3; methyl vinyl ketone, 78-94-4; 1-pyrrolidino-4,4-dimethyl-1-cyclohexene, 41172-02-5.

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